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FULL PAPER

Study of some chemical properties for imported frozen shrimp available in local markets

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This research was conducted to study some chemical properties of frozen shrimp available in local markets, 24 samples were randomly collected for six imported commercial brands from Baghdad city markets, qualitative chemical tests were carried out, which included the values of pH, total volatile nitrogen (TVN)and thiobarbituric acid (TBA), heavy metals lead, cadmium and nickel were estimated, the results showed that there were significant differences at the level of ($P \leq 0.05$) in the values of TVN and TBA, the samples S1 and S3 exceeded the acceptable limits for TVN, reaching 33.28 and 32.71 mg N/100gm, TBA values for all shrimp samples were within the acceptable limits approved by Codex, with the highest value being 1.76, there were no significant differences between shrimp samples in the pH values, which ranged between 7.02 - 7.53, the concentrations of lead, cadmium and nickel elements recorded significant differences at the level ($P \leq 0.05$). Samples S1 and S3 exceeded the acceptable limits for lead approved by Codex, which amounted to 0.337 and 0.660 mg/kg, while cadmium contents (0.082-0.142) were within Codex's (1 mg/kg) guidelines, they were greater than the European Commission's (0.05 mg/kg) permitted levels., all shrimp samples under study were within the acceptable limits for the element nickel.

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KEYWORDS

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Introduction

Shrimps are highly nutritious and expensive marine organisms that are caught or raised in ponds in coastal tropical areas with warm waters, because they are a good source of high-quality proteins, they play a significant function in the diets. Fats, and vitamins and also contain a lot of nutrients and minerals such as calcium, iron [1]. Due to its distinctive flavor and high nutritional value, the demand for it has increased globally and its commercial value has increased, especially in the importing countries. The rate of shrimp production is 6 million tons annually. Asia occupies the lead in its production at a rate of 4.6 tons annually, the value of shrimp exports to the United States reached 1120 million pounds in 2013, while the value of shrimp production in China reached 5314 million pounds in 2011 [2]. Shrimp are exposed to bacterial and chemical contamination and the effect of enzymatic activity during processing, packaging, transportation and storage, which leads to the appearance of undesirable flavors and this turn, affects the sensory qualities of shrimp and thus decreases its nutritional and commercial value [3]. The extent of freshness and safety of shrimp for consumption is determined by phenotypic characteristics, chemical analysis and microbial load estimation. Shrimp are kept by freezing to preserve sensory and quality characteristics and increase their shelf life. However, some enzymatic and chemical reactions occur, including the oxidation of fats and proteins in the tissues, which leads to the deterioration of the sensory characteristics of the product, such as the appearance of an unpleasant odor, rancidity, dehydration, weight loss, color and tissue change [4]. The oxidation of fat during freezing storage is one of the most important reasons for the deterioration of flavor in shrimp and it occurs because its tissues contain a high percentage of unsaturated fatty acids, as well as an interaction between the secondary products of fat oxidation with proteins, which leads to changes affecting the texture, flavor and nutritional value of the product [5]. In addition to the above, shrimp may be contaminated with some heavy metals, either because of the contamination of the water bodies from which they are caught with those metals as a result of industrial waste residues and mining operations whose toxic effects reach the coastal areas of the seas and oceans, or because of additives and preservatives during manufacturing in which fish and marine products are treated, which would extend the shelf life and impart the desired sensory qualities such as flavor and color [6]. Extent of pollution, marine system with heavy metals can be measured by determining their concentrations in water, sediments and marine organisms, which is considered as a dangerous indicator that threatens human life because it affects the ecosystem as a whole and constitutes a source of great concern, this requires adherence to total quality management systems and environmental safety and their full application, especially in developing country [7]. [8] when studying the contamination of the Iraqi sesame product with heavy metals, and [9], who studied the pollution of the Nile river water in Egypt and [10], when they studied the contamination of poultry eggs, proved the presence of heavy metals in various foods, including plants and animals, which are linked to soil, air and water pollution and their cumulative effects in tissues may lead to the emergence and development of some serious diseases to human health, such as reduced immunity, hypersensitivity to chemical agents, various types of tumors and cancer and significant effects on the respiratory, nervous and liver systems, kidneys, fetal growth and development, infertility, in view of the availability of imported frozen shrimp in the Iraqi local markets and the increasing desire to eat it by consumers, this study aimed to measure some chemical characteristics in this product, which may affect its sensory qualities and nutritional value as well as health effects.

Materials and methods

Sample collection

The study included the examination of 24 samples of six brands of imported frozen shrimp, the details of which are shown in Table 1, which were randomly collected from Baghdad city markets during the period from April - October of 2021, they were kept freezing at -18° C until the required tests were performed after the information was established required.

TABLE 1 details of imported frozen shrimp samples

Sample code	No. of Sample	Trade mark	Country of origin	Product date	Expire date
S1	4	Mersin	Turkey	13/10/2021	**12/7/2022**
S2	4	Asmak	United Arab Emirates	16/5/2021	**15/1/2022**
S3	4	Nabil	United Arab Emirates	2/6/2021	**1/2/2022**
S4	4	Osean	United Arab Emirates	12/6/2021	**11/2/2022**
S5	4	Cahta Gpemop	Belarus	4/4/2021	**4/1/2022**
S6	4	Maydar	Bahrain	9/9/2021	**8/6/2022**

Chemical analytics

pH measurement

The method mentioned by [11] was followed, 10 g of sample was weighed and homogenized in an electric mixer by adding 50 mL of distilled water, filtered by Whatman No.1 filter paper and then the pH was read using pH Meter.

Determination of total volatile nitrogen (TVN)

Estimate the total volatile nitrogen according to the method mentioned in [12] by taking 10 gm of shrimp and placing it in a plastic bag, adding 50 mL of distilled water and mixing well using a Stomacher blender, then it was transferred to the distillation flask and 250 mL of distilled water was added to it to complete the volume to 300 mL, 2 g of magnesium oxide and a boiling stone were added, connect the distillation flask to the Kjeldahl apparatus which ends in the receiving flask in which 25 mL of boric acid (2%) with two drops of Methyl Red, after heating and the start of distillation, the dripping mixture was taken after 25 minutes and wiped with sulfuric acid H_2SO_4 (0.1 N). The amount of total volatile nitrogen (TVN) was calculated on the basis of mg nitrogen/100 g of the sample as in the equation:

$$TVN = \frac{(ML\ of\ 0.1\ N\ of\ H_2SO_4) \times 14}{Wt.\ of\ sample\ (g)}$$

Determination of Thiobarbituric acid (TBA)

The method [12] was used by preparing the TBA reagent by dissolving 0.2883 gm of it in 90% icy acetic acid solution and using quiet heating in a water bath to accelerate the dissolution and complete the volume to 100 mL, 10 gm of shrimp was taken and mixed with 47.5 mL of distilled water, 2.5 mL of hydrochloric acid (HCl) (4 N) was added to it to adjust the pH to 1.5, the volume was completed to 100 mL, the contents of the volumetric flask were transferred to the 500 mL distillation flask and a boiling stone was added to it, connect the device and heat using an electric heater until 50 mL of the distillate is collected within 10 minutes. Take 5 mL of the distillate and mix with 5 mL of TBA reagent in a glass test tube with a tight seal, at the same time, blank's solution was prepared by taking 5 mL of distilled water with 5 mL of the reagent. The tubes were closed, shaken, and then placed in a boiling water bath for 35 minutes. The tubes were cooled for 10 minutes, and then the absorbance was measured by a Spectrophotometer at a wavelength of 538 nm according to the acid number TBA mg Malonaldehyde /kg of meat according to the following equation:

$$TBA = 7.8 \times Absorbance$$

Sample digestion and determination of heavy metals concentrations Pb, Cd and Ni

Following the procedure described by [13], the samples were digested to evaluate the concentrations of heavy metals lead, cadmium, and nickel, by drying shrimp samples in an oven at 110° C for 48 hours, then it was turned into a powder using a clean laboratory mill, 2 g of each sample was placed separately in a glass beaker and it was digested by adding 2 mL of nitric acid and 1 mL of chloric acid, it was placed on a hot plate at 120°C and stirred continuously for 3 hours or until the digestion process was completed after the rise of clean white smoke, the digested samples were diluted with distilled water within the range of standards on the basis of which the standard solutions of the minerals to be measured were prepared and according to the instructions of the supplying company, then the concentrations of heavy metals were estimated using Shimadzu AA-6200 supplied with ASC 6100 auto sampler atomic absorption spectrometer equipped with acetylene gas.

Statistical analysis

The statistical program [14] was used, in analyzing the data of the results obtained for chemical tests of shrimp samples, the significant differences between the means were compared with the least significant difference (LSD) test (Analysis of Variation-ANOVA) with probability ($P<0.05$).

Results and discussion

Qualitative chemical tests

pH value

The pH value affects the estimation of the organoleptic characteristics of meat in general, including shrimp, such as color, juiciness and tenderness, as well as its effect on cooking parameters and water carrying capacity [3]. The results of the study showed, as shown in Table 2, that there were no significant differences at the level ($P\leq0.05$) in the pH values between shrimp samples, and sample S5 recorded the lowest pH value of 7.02, while the highest values were 7.53 and 7.51 in samples S1 and S3 respectively, these values are considered a little high and warn of the beginning of the deterioration of the sensory characteristics of these samples, as [1] indicated that the acceptable pH value in marine products ranges between 6.5-7.5, and when exceed these values, the basal characteristic begins to appear and values up to 8 soon effect on the organoleptic and physical characteristics of those products, the pH value varies directly after hunting according to the type, hunting methods and seasons of the year, it naturally decreases hours after death when the anaerobic bacteria begin to produce lactic acid, but it quickly begins to rise due to the secondary metabolites of microorganisms during the freeze storage period [15]. The averages of the pH value in the study of [3], which examined the chemical properties of shrimp samples in Sulaymaniyah city in northern Iraq, were slightly higher than what the results of the current study showed, this value ranged between 7.15-8.36, while the results of the study [16] and [5] converged with what this study found, the pH value was 7.6 in the first study conducted on shrimp samples in Denmark and 7.5 in the second study in Egypt.

TABLE 2 Comparison between frozen shrimp samples in PH, TVN and TBA values

Samples	Mean ±SE		
	pH	TVN mg N/100 gm	TBA mg MDA/kg
S1	7.53±0.42	33.28±1.07 a	**1.37±0.08 ab**
S2	7.04±0.33	16.2±0.75 d	**0.93±0.05 cd**
S3	7.51±0.47	32.71±1.39 a	**1.76±008 a**
S4	7.31±0.25	18.25±0.85 cd	**0.65±0.03 d**
S5	7.02±0.31	27.14±1.08 b	**0.95±0.06 cd**
S6	7.05±0.34	21.55±0.87 bc	**1.23±0.08 bc**
LSD value	0.681 NS	5.063 *	**0.417 ***

Letters in same column differed significantly. * (P≤0.05).

Total volatile nitrogen TVN

Table 2 shows the results of testing the value of the total volatile nitrogen TVN, the shrimp samples recorded values that ranged between 16.22 in sample S2 and 33.28 mg N/100gm in sample S1, and there were significant variations between those samples at the level (P0.05). According to the Codex Alimentarius Commition [17], the acceptable level of TVN for fish and marine products should not be more than 30 mg N/ 100gm, based on these criteria, the shrimp samples under study S1 and S3 exceeded the acceptable limits, recording 33.28 and 32.71 mg N/100gm, respectively, the results of the study of [5] in Egypt came close to what was found by this study, where the values of TVN ranged between 18.2-28.6 mg N/ 100gm, those values increased in the study of [3] from the results of this study, to range between 21.5-46.0 mg N/100gm, while shrimp samples in the study of [16] in Denmark, recorded a clear decrease in the value of TVN amounting to 11.7-16.2 mg N/100gm, TVN is commonly used as an alternative to measuring TMA(trimethylamine) content because TVN mainly contains components such as ammonia, trimethylamine and dimethylamine [4].

Thiobarbituric acid (TBA) value

The results of the TBA value (Table 2) showed that there were significant differences at the level ($P \leq 0.05$) between shrimp samples, as sample S3 recorded the highest TBA value of 1.76 mg MDA/kg and sample S4 the lowest value of 0.56 mg MDA/kg, Shrimp are considered acceptable when the value of TBA is less than 2 mg MDA/kg according to the international standards [16]. The value of this acid rises at the beginning of the process of storing marine products by freezing as a result of the accumulation of fat oxidation products, including the formation of the compound (MDA malonaldehyde) and then begins to decrease as a result of the interaction between this compound and proteins, amino acids, glycogen and others, which leads to a decrease in the percentage of free MDA and the process of malonaldehyde formation during the oxidation of fats intersects with the presence of proteins, which leads to the formation of aggregates of insoluble proteins [11]. [5] indicated in his study of the specific characteristics of Mediterranean shrimp during different freezing periods has a significant effect in raising the value of TBA, its value increased from 0.62 mg N/ 100gm in the control before freezing to 0.87 mg N/ 100gm after a month of freezing and 1.69 mg N/100 gm after 6 months, while [12] indicated that the use of antioxidants such as tri-sodium phosphate with different concentrations led to a decrease in the rate of MDA formation and thus a decrease in the concentration of TBA, whose high concentrations (above 2 mg N/ 100gm) caused the appearance of rancid smell and taste, for frozen shrimp, the concentrations of TBA remained within the acceptable limits, the control sample before freezing recorded 0.48 mg N/100gm to rise to 2.73 after freezing for 6 months, while the sample treated with antioxidant maintained the value of 1.87 after the passage of the same period and it is worth noting that the TBA value for all shrimp samples is under the study was within acceptable limits.

Estimation of heavy metals

Lead

Table 3 shows the concentrations of heavy metals in the shrimp samples under study, the lead concentrations showed significant differences at the level ($P \leq 0.05$). Samples S1 and S3 recorded the highest concentrations of this element, which amounted to 0.377 and 0.660 mg/kg, respectively, it is higher than the acceptable limits for lead in marine products approved by international standards [17], which does not exceed 0.3 mg/kg, while the rest of the shrimp samples under study remained within the acceptable limits, lead poisoning in humans leads to poor learning abilities, affects immunity by interfering with the function of white blood cells, and increases the possibility of chromosomal aberrations during the cell division process, which leads to mutations [18].

TABLE 3 Comparison between frozen shrimp samples in heavy metals concentrations

Samples	Mean±SE		
	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)
S1	0.377±0.04 b	0.132±0.02 ab	**0.041±0.01 a**
S2	0.103±0.02 d	0.082±0.02 b	**0.000±0.00 b**
S3	0.660±0.06 a	0.125±0.03 ab	**0.015±0.01 ab**
S4	0.037±0.04 cd	0.121±0.04 ab	**0.013±0.01 ab**
S5	0.298 ±0.04 bc	0.100±0.01 ab	**0.000±0.00 b**
S6	0.235±0.03 bc	0.142 ±0.04 a	**0.018±0.01 ab**
LSD value	0.198 *	0.058 *	**0.0327 ***

Means in same column differed significantly. * (P≤0.05).

The results of the study of [19] and [17], approached the results of this study, as the concentrations of Pb in shrimp samples in the first study, which were caught from the coast of the Congo, ranged between 0.354-0.691 mg/kg and in second 0.12- 0.46 mg/kg for shrimp in Bangladesh, while [20] also in Bangladesh, found the concentrations of lead were very low in the frozen shrimp samples collected from the capital markets, ranging between 0.065-0.087 mg/kg, [21] mentioned when studying the concentration of heavy metals in shrimp caught from the waters of the Islamic Republic of Iran in the Persian Gulf in 2012, the concentration of lead was 1.539 mg/kg, it is worth noting that four samples of shrimp under study were S2, S3, S4, S6 it is caught from the waters of the United Arab Emirates and Bahrain in the Persian Gulf.

Cadmium

Chronic exposure to cadmium may lead to an imbalance in the liver and kidneys, impede the building and repair of bones, and increase the incidence of tumors and bladder cancer [22], the shrimp samples under study recorded concentrations of cadmium (Table 3) that ranged between 0.082 in sample S2 and 0.142 mg/kg in sample S6 and there were significant variations between those samples at the level (P0.05), the Codex standard [23], specified the proportion of cadmium in marine products as no more than 1 mg/kg, while the European commission regulation [24] approved a maximum rate of 0.05 mg/kg for cadmium in marine products, cadmium concentrations in shrimp samples under study deviated from the acceptable limits by Codex, and were lower than them, but they exceeded the limits set by the European Standard, the results of the study of [18] approached the concentration of cadmium in Egyptian shrimp caught on the coasts of the Mediterranean, reaching 0.12- 0.15 mg/kg, while cadmium concentrations were low in studies of [21], in Iran and [17] in Bangladesh, they were 0.057 and 0.049 mg/kg, respectively.

Nickel

Returning to Table 3, which shows the concentrations of nickel in shrimp samples, there were significant variations between those samples at the level (P0.05), the element's concentration ranged between 0.013-0.041 mg/kg in samples S4 and S1, respectively, while its concentration was very low, the examination device did not detect it in samples S2 and S5, it's worth mentioning that the nickel amounts in all of the shrimp samples studied were within the Codex standard's allowed range [21], that the nickel concentration in marine products does not exceed 1 mg/kg, studies of [17], [20] and [19] were recorded nickel concentrations similar to the samples of current study, which amounted to 0.042 in Bangladesh, 0.048 in Congo, and 0.021 mg/kg in Egypt for the three studies, respectively, while [13] recorded very low nickel values for shrimp in the Nigerian capital Lagos, which amounted to 0.0026. mg/kg.

Conclusion

Chemical characteristics are an indicator of the quality of frozen shrimp; it greatly affects its sensory characteristics. The results showed that the pH values were relatively high, although they are within the acceptable limits, but the TVN values of two brands exceeded the acceptable limits, which indicates the beginning of the deterioration of their sensory characteristics with TBA values is kept within acceptable limits. The values of lead were significantly higher in some samples, and cadmium concentrations approached the highest permissible limit, which indicates the environmental deterioration of some water bodies with these elements. Therefore, it is necessary to control pollution by adopting appropriate strategies to prevent and reduce the toxicity of heavy metals.

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